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DECONTAMINATION SYSTEM UTILIZING HYDROGEN PEROXIDE, UV LIGHT AND CATALYTIC SURFACES

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Vineburg, CA 95487

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A decontamination process utilizing condensing 50% hydrogen peroxide vapor and 254 nm ultraviolet (UV) light was tested in the laboratory utilizing several agent simulants. The UV light photolyzes hydrogen peroxide, producing hydroxyl radicals which react rapidly with most organic molecules. The rate of reaction is determined mostly by the solubility of the agent simulant in the water-like hydrogen peroxide condensate. The insecticide Dimethoate, a simulant for Agent VX, is effectively destroyed due to relatively high water solubility. Phenyl half-mustard and Malathion are much less soluble in water, and only partial decontamination was achieved. Material damage is a major concern. Several conformal coatings and two paint systems were tested. Some performed well, but others failed rapidly.

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PREFACE

The work described in this report was authorized under Contract No. DAAA15-90-C-1005. This work was started in July 1990 and completed in April 1991.

The use of trade names or manufacturers' names in this report does not constitute an official endorsement of any commercial products. This report may not be cited for purposes of advertisement.

Acknowledgments

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The coated circuit boards used to test the resistance of conformal coatings were provided by Dr. Olexander Hnojewyj of Litton Applied Technologies (Santa Clara, CA).

The sample of unformulated, technical grade dimethoate used was provided by the FMC Agricultural Chemicals Group (Fresno, CA).

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DECONTAMINATION SYSTEM UTILIZING HYDROGEN PEROXIDE, UV LIGHT AND CATALYTIC SURFACES

INTRODUCTION

This project was initiated July 30, 1990 to investigate a decontamination system utilizing condensing hydrogen peroxide vapor and either UV light or catalytic surfaces. This is a non-selective system for use inside of vehicles or similar enclosed spaces, and designed to be carried by the vehicle. Fifty percent hydrogen peroxide is applied as a vapor which condenses upon all surfaces reached by the vapor. Some chemical agents and many biological agents are deactivated by direct, uncatalyzed reaction with H_2O_2. To induce non-selective reaction of H_2O_2 with practically all chemical agents, irradiation with UV light and reaction with catalytic surfaces were tested as a means of converting part of the H_2O_2 to hydroxyl radicals.

Hydroxyl radicals are extremely reactive. The dissociation energy of the HO-H bond is 121 kcal while aliphatic C-H bonds (excluding methane) range from 91-98 kcal. The enthalpy change for the reaction

$$(1) \quad R\text{-}H + HO^{\cdot} \longrightarrow R^{\cdot} + H_2O$$

ranges form -23 to -30 kcal and the entropy change is usually near zero. Therefore, $OH^{\cdot}$ will readily abstract any aliphatic hydrogen atom, converting the stable substrate to a reactive organic free radical. Agents containing reduced sulfur may be preferentially attacked at the sulfur atom. Practically all organic compounds are attacked by $OH^{\cdot}$ (Anbar and Neta 1967).

The free radicals created by attack of $OH^{\cdot}$ on organic molecules will react further with O_2 or H_2O_2 in a chain reaction; therefore, several molecules of organic substrate may be affected by the reaction sequence initiated by a single hydroxyl radical (Merz and Waters 1949, Walling and Kato 1971).

Once an agent is dissolved in H_2O_2/H_2O, it will be rapidly degraded by reaction with $OH^{\cdot}$, H_2O_2 and O_2. Therefore, the time required for decontamination will be determined largely by mass transfer kinetics; specifically, by the rate of solution of the agent in the liquid film of H_2O_2/H_2O.

Hydrogen peroxide is less corrosive than other volatile decontamination agents (e.g., ASH vapor, HOCl). In the absence of strong acids or bases, most materials are unaffected by dilute H_2O_2, while H_2O_2 in the 50% range is corrosive to some materials. Corrosion by H_2O_2 is self-limiting, because many surfaces catalyze the decomposition of H_2O_2 to water and oxygen.

The following processes were investigated to determine their ability to degrade hypotoxic agent simulants representing GD, GB, VX and HD:

1) Exposure to condensing H_2O_2/H_2O vapor alone
2) Exposure to condensing H_2O_2/H_2O vapor plus UV light
3) H_2O_2/H_2O vapor on catalytic surfaces.

Additionally, several surfactants were tested for their ability to improve wetting behaviour and mass transfer of agent simulants.

Resistance of electronic equipment to damage by H_2O_2 will be determined by how susceptible the conformal coatings are to damage by H_2O_2. Several Mil-Spec circuit boards coated with a variety of Mil-Spec conformal coatings were exposed to condensing H_2O_2 vapor, then examined for visible damage.

This report is a summary of the research including 1) a description of the experimental equipment and its performance, 2) an evaluation of agent simulants, and 3) a discussion of the results obtained.

EXPERIMENTAL PROCEDURES

Test Chamber

An experimental apparatus was designed consisting of two test chambers, one inside of the other (Figures 1a, 1b). The outer test chamber is a portable, bench-top hood with walls fabricated of transparent acrylic plastic for maximum visibility, with dimensions 23x30". The inner test chamber is basically an aluminum box 11x12x18 inches, with transparent acrylic windows in three sides. The actual experiments are set-up and performed in the inner chamber, which has the ultraviolet lamps installed at its top. The inner chamber contains most of the UV light, and

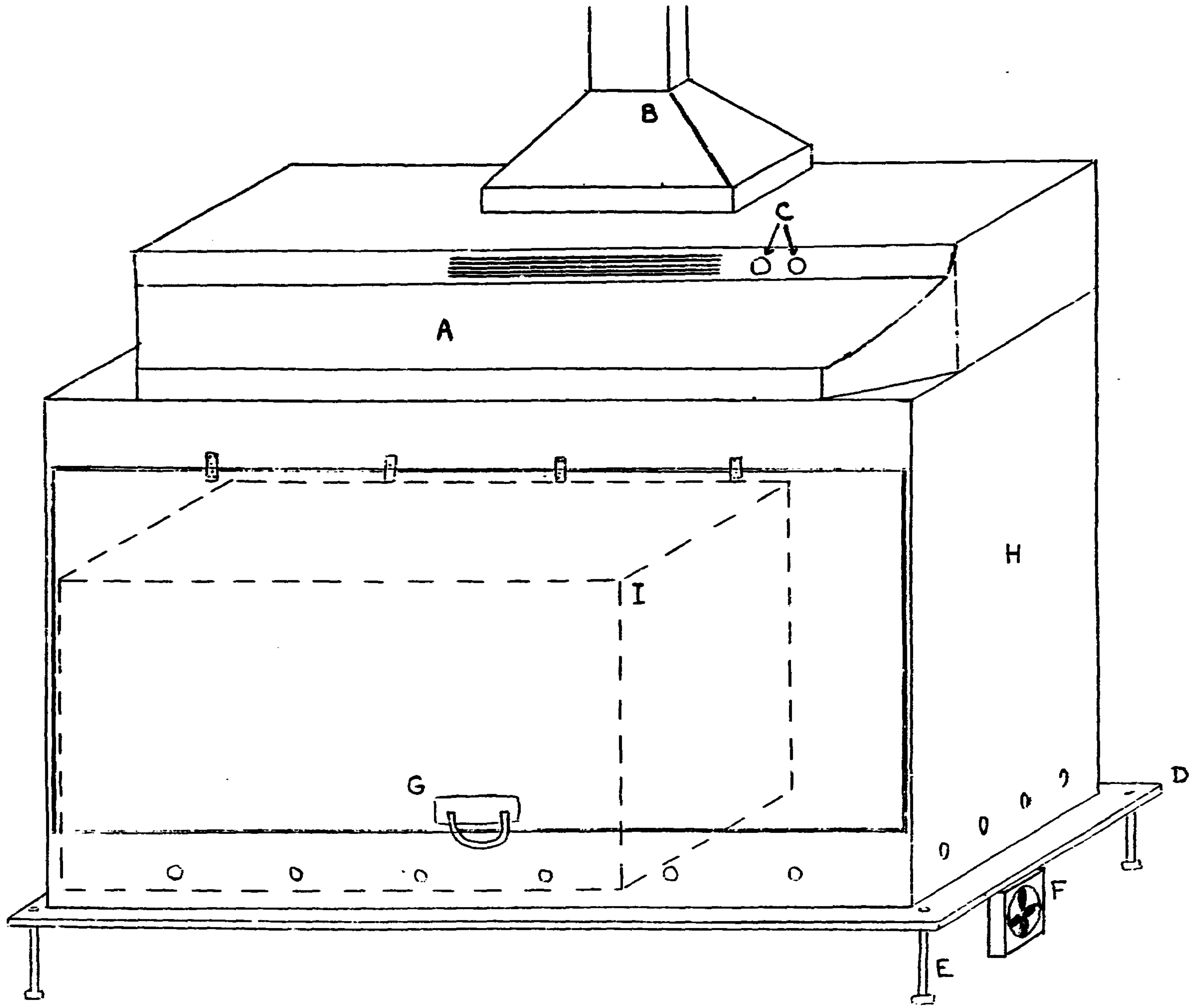


Figure 1a. Outer Chamber

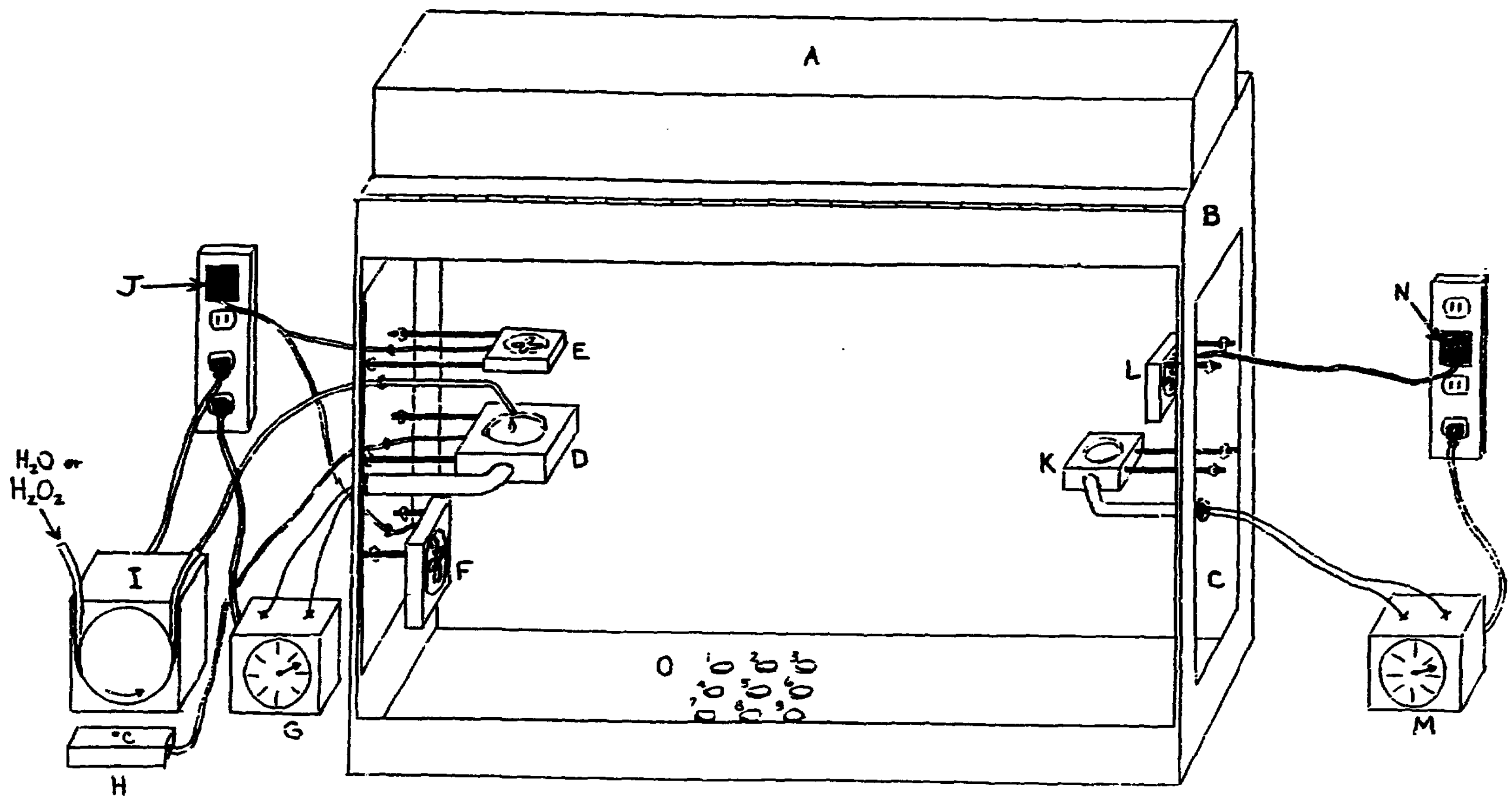


Figure 1b. Inner Chamber (Front Door Removed)

Notes to Figure 1a.

A. Nautilus Microtek System III kitchen hood.
B. Hood exhaust vent.
C. Hood controls.
D. 1/4 inch aluminum plate serves as floor of both chambers.
E. 5 inch high legs elevating floor.
F. 65 cfm compact fan keeps aluminum plate cool for maximum condensation on floor of chamber.
G. Brass handle on Plexiglass door of chamber.
H. Plexiglass sides with vent holes.
I. Dashed lines represent location of inner chamber. See Fig.1b.

Notes to Figure 1b.

A. Aluminum box containing four 16W UV lamps radiating approximately 21W of UV energy, mostly at 254 nm. The intensity of UV light measured at the floor of the test chamber in the absence of condensate is 5.1 mW/cm^2.
B. Aluminum walls of inner chamber.
C. Plexiglass windows of inner chamber.
D. Primary heated aluminum block for evaporating hydrogen peroxide or water.
E. 4.6 cfm compact fan to aid evaporation.
F. 27 cfm compact fan for dispersing evaporated liquid.
G. Temperature controller for primary heated aluminum block.
H. Digital thermometer.
I. Precision peristaltic pump.
J. AC adapter for compact fans.
K. Auxiliary heated aluminum block for evaporating agent simulants.
L. 4.6 cfm compact fan to aid in evaporation of simulants.
M. Temperature controller for auxiliary heat block.
N. AC adapter for compact fan.
O. The floor of the chamber is stamped with the numbers 1 to 9 for consistent placement of the test disks. The numbers are in 3 rows of 3 numbers each in the shape of a square near the center of the chamber.

Note: Vinyl tape is used to seal the base of the inner chamber to the aluminum plate that forms the floor. Masking tape is used to seal the front door closed. The front door (not shown in Fig.1b.) is a 1/8" aluminum plate with a Plexiglass window in it.

the portable hood (the outer chamber) will keep hydrogen peroxide vapors and traces of agent simulant from getting into the room air.

Four lamps (Slimline Germicidal Lamp, G10T5 1/2 L, Light Sources, Inc., Milford, CT) are installed, drawing a total of 64W and radiating approximately 21W of UV energy, mostly at 254 nm. The intensity of UV light at 254 nm, measured at the floor of the test chamber near its center in the absence of condensate, is 5.1 mW/cm^2.

Both chambers are open at the bottom and are placed upon a platform of 0.25" aluminum plate that is raised approximately 5" above the benchtop. Test coupons are placed directly on the aluminum plate, inside the inner chamber. Air blown underneath the aluminum plate by a compact 65 cfm fan keeps the plate near ambient room temperature. The cool plate serves as a heat sink, causing condensation of hydrogen peroxide upon the test coupons.

Hydrogen peroxide vapor is provided by evaporating stabilized 50% hydrogen peroxide on a heated aluminum block exposed to flowing air. A temperature controller allows the temperature of the block to be maintained within an interval of 2°C. The block is kept at about 127°C when evaporating hydrogen peroxide and about 109°C when evaporating water. With these settings and a liquid feed rate of 1 mL/min or less, the wetted area of the block is 1 cm^2 or less, and we estimate the residence time of the liquid on the heated block to be less than five seconds.

A small fan (4.6 cfm) mounted directly above the heated block helps evaporate the hydrogen peroxide, and a larger fan (27 cfm) mounted horizontally below the block rapidly disperses the hydrogen peroxide vapor throughout the volume of the chamber, promoting uniform condensation on the bottom of the chamber. The heaviest condensation of hydrogen peroxide occurs on the bottom of the test chamber. The blank back of the test chamber, plus parts of the top and sides have been insulated using 0.125 inch thick adhesive foam insulation of the kind applied to water pipes. Most of the top surface of the chamber is warm due to the UV lamps and their ballasts, and the Plexiglass windows are naturally poor heat conductors. When necessary to improve visibility, the windows are heated from the outside using a blower-type hair drier to inhibit condensation. These measures cause 55% of the total condensate (see 'Evaporation of hydrogen peroxide in the test chamber' below) to form on the floor of the chamber, which constitutes only about 20% of its internal area.

A second heated aluminum block with temperature controller is installed in the inner chamber opposite the first heated block, and is dedicated to evaporating agent simulant as needed to saturate the chamber atmosphere. This enables improved control of agent simulant concentrations in air in experiments utilizing relatively volatile compounds, such as 2-chloroethyl phenyl sulfide (phenyl half-mustard, PHM) and diisopropyl methylphosphonate (DIMP). A small fan (4.6 cfm) is horizontally mounted directly above the heated block to aid in the dispersion of the agent simulant vapor throughout the volume of the chamber.

Tube and electrical connections enter the test chamber through ports drilled in the plastic windows. The ballasts and wiring for the UV lamps are installed outside of the inner chamber, in an attached compartment designed to provide the required degree of electrical safety.

Evaporation of Hydrogen Peroxide in the Test Chamber

A preliminary experiment was performed to determine if, indeed, hydrogen peroxide can be boiled on a heated aluminum block without excessive decomposition. Hydrogen peroxide was evaporated on the block, and condensed on the air cooled bottom plate of the test chamber, and inside of a tared Petri dish placed inside the chamber. After thirty minutes the Petri dish was weighed and a known amount of water was added to it to dilute the condensate. The 50w% hydrogen peroxide solution used was also diluted, and both were analyzed by measuring UV absorption at 300 nm. It was determined that the condensate in the Petri dish contained approximately 40w% hydrogen peroxide. Allowing for the fact that the hydrogen peroxide feed lines were filled with water at the start of the experiment, this result indicates that 80% of the hydrogen peroxide survives boiling and condensation. The weight of the condensate collected in the Petri dish indicated that approximately 55% of the hydrogen peroxide condensed on the bottom of the test chamber. Another, different experiment employing water confirmed this estimate.

Test Coupons, Paints and Material Performance

The test coupons used in our experiments are 0.625 inch diameter metal disks, coated using the appropriate Chemical Agent Resistant Coating (CARC) System paints. Hot-rolled steel disks were coated with MIL-P-52192B two-part epoxy primer and MIL-C-53039 polyurethane top coat. Primer only was applied to one side, both primer and top coat to the other. The aluminum disks were painted on one side only using MIL-P-233377E two-part epoxy primer plus the same polyurethane top coat. The steel primer is red-brown, indicating that it contains hematite pigment. The aluminum primer is pale yellow, suggesting a chromate pigment.

The area of the disk is 1.98 cm^2. A 1 microliter drop of agent simulant is applied to the disk with a chromatography syringe, and spread out with a fine wire to cover a circle of approximately 0.5 inch = 1.27 cm diameter, with area = 1.27 cm^2. In the case of Malathion (SG = 1.20) this corresponds to a surface loading of 9.5 g/m^2.

Exposure to 50% hydrogen for 30 minutes severely damaged the steel primer. Exposed primer swelled badly, and primer plus top coat on steel blistered badly, allowing the top coat layer to be peeled off. It is likely that the hematite pigment in the primer catalyzed decomposition of hydrogen peroxide that diffused into the paint, and perhaps catalyzed chemical attack of hydrogen peroxide upon the paint resin. These reactions severely damaged the primer coat.

Upon one hour exposure to 50% hydrogen peroxide, a coat of yellow primer only on aluminum blistered with no other visible damage. The blistering probably was caused by evolution of oxygen bubbles beneath the paint membrane, and allowed the paint easily to be peeled from the disk as an intact circle, leaving spotlessly clean metal. Inadequate surface preparation (particularly degreasing) may have been a contributing factor.

Aluminum disks with both primer and top coat suffered no visible damage after 75 minutes of exposure to 50% hydrogen peroxide, with or without UV light. Evidently, the polyurethane top coat is unaffected by hydrogen peroxide, and is able to protect the aluminum primer, probably by blocking diffusion of hydrogen peroxide into the paint membrane.

After about three hours of exposure to condensing hydrogen peroxide and UV light, unpainted aluminum surfaces inside the test chamber were slightly corroded, and a small amount of solid corrosion products may be wiped from the metal, leaving a lightly mottled surface. The Plexiglass windows of the test chamber became crazed. According to the manufacturer of the UV lamps, crazing of polyacrylate can be attributed to UV exposure alone.

Fumed Silica Powders

Uniform distribution of H_2O_2/H_2O on the test disks presents a problem. The surface tension of 50% H_2O_2 is similar to that of water, and drops of H_2O_2/H_2O form "beads" when applied to most surfaces. Agent deposited on the surface may aggravate this tendency by producing a smooth, hydrophobic surface coating. Our

experiments confirmed that a surfactant is needed to provide uniform coverage of the surface by condensing H_2O_2.

A surfactant for this application should (a) not impart electrical conductivity, (b) have some degree of resistance to oxidation by $OH^{\cdot}$ and H_2O_2, and (c) should not produce corrosive residues if oxidized. Partially hydrophobic particles of colloidal silica congregate at liquid-vapor and liquid-liquid interfaces, and have a powerful surfactant effect (Iler 1979, p. 594). High temperature dehydration renders silica hydrophobic, and long exposure to water is required to reverse the effect (Ibid., pp. 661-663). Dehydrated particles of amorphous silica would be ideal for this application because they are nonconductive, immune to oxidation, will not absorb UV light, and will not release corrosive chemical residues. In principle, silica dust can cause silicosis, but amorphous silica is less toxic than quartz, and the silicosis hazard may be largely eliminated by avoiding the respirable size range, 0.5-5.0 microns (Ibid., p. 774).

A rough surface will provide more nucleation sites for droplets of condensate, and will thereby favor the accumulation of a more uniform condensate layer than would a smooth surface. Surfaces coated with catalytic oxide particles will be rough by virtue of the particles imbedded in them. In practice, silica powder applied to the surface adheres in fairly coarse clumps, thereby roughening the surface and promoting uniform nucleation as well. As a rule, very many small droplets of condensate form on a silica coated surface, approaching a uniform distribution.

Six fumed silica powders and one liquid surfactant (Table 1) were tested for their ability to enhance the uniform condensation of hydrogen peroxide on surfaces wetted with agent simulants and, therefore, provide more efficient mass transfer of agent simulant into solution. The powders were obtained as commercial samples from Cabot and Degussa. Each of them is a dry powder consisting of amorphous silica particles of colloidal size (ultimate particle diameter around 10 nm, specific surface area around 200 m^2/g). Four of these are hydrophilic silicas, with hydroxylated surfaces, and two are hydrophobic silica, with silylated particle surfaces. The liquid surfactant is a nonionic product sold as an emulsifier for pesticides by the DeSoto Chemical Company, probably a polyethoxylated phenol.

Gas Chromatography

A Tracor 540 gas chromatograph with a flame photometric sulfer/phosphorus detector (FPD) with an integral flame

Table 1.

Fumed silicas tested for their ability to provide uniform condensation and improved mass transfer of agent simulant

Silica	Type	Manufacturer
Aerosil 200	Hydrophyllic powder	Degussa Corp.
Sipernat 22 LS	Hydrophyllic powder	Degussa Corp.
Cab-O-Sil Grade EH-5	Hydrophyllic powder	Cabot Corp.
Cab-O-Sil Grade M-5	Hydrophyllic powder	Cabot Corp.
Aerosil R974	Hydrophobic powder	Degussa Corp.
Cab-O-Sil TS-610	Hydrophobic powder	Cabot Corp.
FloMo 9N	Surfactant solution	DeSoto Inc.

ionization detector (FID) was used for the analysis of agent simulants. A 6' x 0.25" O.D. glass column with 3% OV-1 stationary phase has been used at 200°C and 50 mL/min argon carrier gas flow for all the agent simulants that were used in our experiments. Chromatography problems were encountered with Acephate, which ultimately led to our abandonment of this simulant, and with Dimethoate. The Dimethoate problem was resolved and is discussed in the 'Experimental Progress' section.

AGENT SIMULANTS

We have evaluated five potential agent simulants in the course of our experiments. Three insecticides, Malathion (Pfaltz & Bauer), Acephate (Chevron), and Dimethoate (FMC Chemicals) have been used as simulants for agent VX. 2-chloroethyl phenyl sulfide (Fairfield Chemical) was used as a simulant for sulfur mustard and diisopropyl methylphosphonate (Johnson Matthey) was used as agent simulant for GB. These compounds are summarized in Tables 2a and 2b.

Malathion

Malathion, a very common dithiophosphate insecticide, is somewhat similar to agent VX in that it contains sulfur bonded directly to phosphorus. Like VX, Malathion has a low vapor pressure, and losses by evaporation during the experiments are negligible. Unlike VX, which has water solubility of 3% at room temperature, Malathion has a water solubility of only 145 ppm, six-fold smaller than sulfur mustard. The low water solubility of Malathion causes the rate of solution of Malathion in the condensing hydrogen peroxide to be small, and mass transfer limits the overall rate of chemical destruction of Malathion.

Acephate

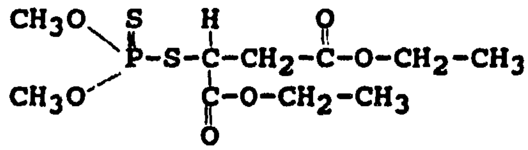
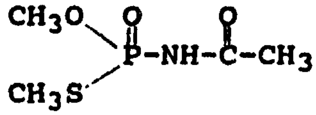
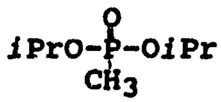
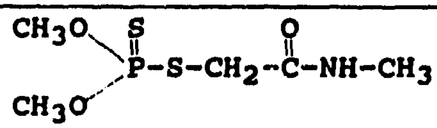
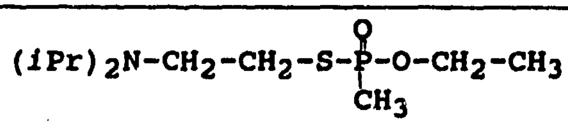
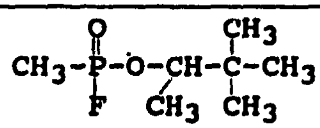
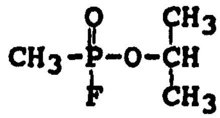
Acephate is very soluble in water (79 g Acephate into 100g water) and exemplifies the extreme opposite case from Malathion. Destruction of Acephate should be controlled entirely by liquid phase reaction kinetics, with little or no effect from mass transfer kinetics.

Severe problems were encountered in attempting to quantify Acephate by gas chromatography (GC). Sometimes the peak is split, and sometimes the Acephate doesn't come out at all. A subsequent injection of solvent then brings out the "lost" Acephate. The combination of high water solubility and very low vapor pressure appears to be the problem. The injected sample rapidly dries down to a droplet of molten acephate, which does not dissolve in the hydrophobic liquid phase in the column.

Table 2a. Summary of Agent Simulants

Agent/Simulant	FW	Vapor Pressure	BP	MP	Water Solubility	Type
Malathion	330.4	1.6×10^{-7} bar @20°C	156°C @ 1 mbar	2.8-3.0°C	145 ppm @25°C	Dithiophosphate insecticide ($C_{10}H_{19}O_6PS_2$)
2-Chloroethyl-phenyl sulfide	172.7	7.6×10^{-5} bar @25°C			168 ppm	(C_8H_9ClS)
Acephate	183.2	2.3×10^{-9} bar @24°C	Decomposes on Distillation	93°C	79g/100ml @20°C	Thiophosphate insecticide ($C_4H_{10}NO_3PS$)
Diisopropylmethyl phosphonate	180.2	3.1×10^{-5} bar @25°C	78°C @10 mm Hg			Phosphonate ($(C_3H_7O)_2P(O)CH_3$)
Dimethoate	229.3	1×10^{-8} bar	117°C @0.13 mbar	51°C	2.5g/100ml	Dithiophosphate insecticide ($C_5H_{12}NO_3PS_2$)
VX	267.4				3.0g/100ml @25°C	Thiophosphonate ($C_{11}H_{26}NO_2PS$)
GD	182.2				2.1g/100ml @20°C	Fluorophosphonate ($C_7H_{16}FO_2P$)
GB	140.1					Fluorophosphonate ($C_4H_{10}FO_2P$)
Sulfur Mustard	159.5				900 ppm	($C_4H_8Cl_2S_2$)

Table 2b. Chemical Structures of Agents and Simulants

Malathion	
2-Chloroethyl-phenylsulfide (PHM)	$Cl{-}CH_2{-}CH_2{-}S{-}\phi$
Acephate	
Diisopropylmethyl phosphonate (DIMP)	
Dimethoate (DMO)	
VX	
GD	
GB	
Sulfur Mustard	$Cl{-}CH_2{-}CH_2{-}S{-}CH_2{-}CH_2{-}Cl$

Evaporation from the relatively small surface area of the droplet is slow, and the injection seems "lost". A subsequent injection of solvent briefly dilutes and redistributes the droplet, causing a spurious peak to appear. We were unable to produce any usable data with Acephate and finally were forced to remove several inches of packing from the injection end of the GC column to get the accumulated Acephate out of it. In addition, Acephate is a solid melting at 93°C, and decomposes fairly rapidly in solution, requiring that fresh solutions be made daily.

Dimethoate (DMO)

This insecticide is a dithiophosphate similar to Malathion; the P/S end of the molecule is identical to the same part of the Malathion molecule. Dimethoate differs from Malathion in having lower molecular weight (229.28) and being more polar. Therefore, Dimethoate is much more water soluble than Malathion, and also less volatile. It is, however, sufficiently volatile to readily be analyzed by GC using the FPD detector. The water solubility of DMO (2.5% at room temperature) is a good match for VX and GD. The low volatility of DMO (10^{-8} bar at 20°C) makes it reasonably safe to work with, and eliminates loss by evaporation during the experiment. Dimethoate is a solid melting at 52°C, but adding 20% glycerol to it keeps it liquid at room temperature. Because it is a dithiophosphate, its susceptibility to oxidation probably is comparable to that of Malathion, and may be somewhat greater than that of VX or GD. Despite these caveats, we consider DMO to be the best simulant for oxidation reactions of VX that we are aware of, because it closely matches the water solubility of VX, and probably also the rate of dissolution in water.

2-Chloroethyl Phenyl Sulfide

2-Chloroethyl phenyl sulfide (phenyl half-mustard: PHM) is believed to simulate the solubility properties of sulfur mustard more closely than Malathion simulates agent VX. Like Malathion, PHM also has a very low water solubility which limits the overall rate of chemical destruction of PHM. Phenyl half-mustard is much more volatile than Malathion, and losses of the simulant by evaporation during the course of our experiments are substantial. In a preliminary experiment utilizing water only with no UV light, the average recovery of PHM from disks with silica powders was only 28%. An attempt was made to decrease evaporation of PHM from the test disks by evaporating sufficient added PHM at the start of the experiment to immediately saturate the atmosphere in the test chamber. Doing so increased the average recovery of PHM from disks with silica powder to 39% (Experiment G). Several air samples were taken during the course of this experiment and analyzed by GC. The peak corresponding to PHM was readily

evident in the chromatogram, and grew slowly as the experiment progressed. A second peak at slightly longer time also appeared and grew much more rapidly, until it was nearly three times larger than the PHM peak. The second peak was probably a decomposition product of PHM, most likely 2-hydroxyethylphenylsulfide produced by reaction with water. This peak was never noted in liquid samples washed from the test disks. The apparent hydrolysis reaction limits the degree to which evaporation can be suppressed by adding PHM vapor to the air in the chamber.

Diisopropyl Methylphosphonate

Diisopropyl methylphosphonate (DIMP) has been commonly used by others as a simulant for GB and probably simulates the vapor phase oxidation chemistry of GB fairly well, and that is the main requirement in this case, because of the high volatility of GB and DIMP. However, the water solubility of DIMP probably is much lower than the solubility of GB.

RESULTS

Experiments Using Malathion

Because Malathion is an organic compound of sulfur, it is a good substrate for oxidation. However, its water solubility is low and the overall rate of reaction will be limited by phase transfer. Three successful experiments have been completed and are summarized in Table 3. In each case nine (9) test disks were exposed to condensing water vapor alone, or condensing hydrogen peroxide vapor and UV light in the test chamber. Eight of the disks were doped with Malathion at approximately 9.5 g/m^2 (within the doped area of the disk). Six of these were further coated each with a different fumed silica powder, and one was lightly sprayed with an aqueous solution of a liquid surfactant. The ninth disk had nothing put on it, and served to test the pattern of condensation on an untreated, painted surface, and possible surface damage. A tenth disk coated with Malathion only was kept outside of the test chamber in a covered container as a control.

The liquid surfactant is applied to the disks as a spray of 2.5% solution in water sufficient to lightly wet the disk. A small jig was devised to evenly and reproducibly apply the powders to the disks. About 3 or 4 mg of silica powder is blown at the disk by a puff of compressed gas with reproducible distance and geometry and approximately 1-2 mg of powder adheres to it. Thus, the amount of silica powder actually deposited on the disk is only 10-20% of the mass of agent simulant.

Table 3.

Malathion Exposed to Hydrogen Peroxide and UV Light

Experiment	B	C	E
Date	10-26	10-27	10-29
Malathion (g/m^2)	10	10	10
Liquid	50% H_2O_2	H_2O	50% H_2O_2
Condensed (g/m^2)	126	106	155
UV Light	yes	no	yes
Run Time (min)	38	38	75

Results:

Disk	Surfactant	Percent	Malathion	Recovered	E/C
1	Aerosil 200	49	73	27	37
2	Sipernat 22 LS	39	56	35	62
3	Cab-O-Sil Grade EH-5	30	75	11	15
4	Cab-O-Sil Grade M-5	28	89	25	28
5	Aerosil R974*	39	62	9	15
6	Cab-O-Sil TS-610*	32	39	12	31
7	FloMo 9N (liquid)	47	--	41	--
8	None	75	104	59	57
Control	No Surfactant	100	100	100	--
Reference Solution		1-3	106	95	--

*These silica powders have been treated to make them hydrophobic; the other four are hydrophyllic.

After the disks were placed inside of the test chamber, the chamber door was sealed with masking tape, the various fans were turned on, and the temperature of the heated block was allowed to stabilize. Then the UV lamps and the liquid pump were turned on, and the experiment was under way.

After the allotted time had elapsed, everything was turned off, the test chamber was opened, and the disks were transferred to small wide-mouth vials. Five milliliters of acetone were added to each vial to extract the remaining agent simulant for quantitative analysis by GC. The acetone contains 40 ppm (v/v) of phenyl sulfide which serves as an internal standard. The FPD is set to detect sulfur, and response is linear up to 40 ppm phenyl sulfide or 200 ppm Malathion.

All results for Malathion recovered are expressed as the percentage relative to that recovered from the control disk, which had Malathion applied to it, and then was kept in a covered container outside of the test chamber. "Reference solution" was prepared to contain 40 ppm phenyl sulfide and 200 ppm Malathion, which corresponds to 100% recovery of the Malathion applied to a test disk. The good agreement between "Reference" and "Control" observed in all cases illustrates the basic precision of the analytical protocol, and demonstrates that Malathion is recovered well from the test disks.

Experiment C was performed using water in place of 50% hydrogen peroxide and no UV light. The purpose of this experiment was to determine how much agent simulant would be lost by evaporation during the experiment or by other spurious mechanisms, instead of through chemical reaction. Disk 8 was coated with Malathion only, with no surfactant, and all of the Malathion was recovered. This result confirms that there is no significant loss by evaporation, as expected considering the very low vapor pressure of Malathion. The incomplete recovery of Malathion from disks dusted with the silica powders was unexpected. We believe that the Malathion was absorbed so powerfully by the silica that soaking the disk in acetone was an insufficiently vigorous treatment to recover all of it.

Experiments B and E were performed with condensing hydrogen peroxide and UV light. In Experiment E, the time of exposure to condensing H_2O_2 and UV light was 75 minutes, approximately double the exposure time in Experiment B. With all surfactants, recovery of Malathion obeys the pattern C > B > E. This pattern indicates that exposure to condensing hydrogen peroxide plus UV light does destroy Malathion by chemical reaction, and longer exposure time increases the extent of reaction. Despite the longer reaction time, we believe that Experiment E may fairly be compared with Experiment C, because the degree of adsorption of

Malathion onto the silica powder should not vary with run time; therefore, recovery after exposure to condensing water vapor should not vary strongly with duration of exposure.

The last column (labeled E/C) presents the percentages from Experiment E divided by the percentages from Experiment C. In effect, the effect of adsorption on to the silica has been corrected for. In two cases, the recovery of Malathion in Experiment E is 85% smaller than with the corresponding surfactant in Experiment C. The presence of fumed silica clearly enhances destruction of the Malathion.

Experiments Using Phenyl Half-Mustard

Phenyl half-mustard is a good simulant for sulfur mustard. It differs from sulfur mustard in being somewhat less soluble in water, and in reacting more rapidly with hydroxyl radical, because it contains a phenyl group. As with Malathion, the overall rate of reaction is limited by mass transfer. In most respects, these experiments were the same as with Malathion described above, however, due to the much higher volatility of (PHM) than Malathion we evaporated 0.06 mL of PHM in a small Inconel cup upon the heated block used to evaporate hydrogen peroxide. This presaturated the chamber with PHM and, theoretically, should limit the amount of PHM evaporating from the test disks. Experiments G and I were performed before the auxiliary heating block was added to the reaction chamber necessitating the use of the Inconel cup. On completion of each of these experiments it was noted that not all of the PHM had evaporated. Experiment AC was performed later using the auxiliary heat block to ensure complete evaporation of the PHM.

Two successful experiments utilizing PHM, experiments G and I, are summarized in Table 4. As with Malathion, in each case nine (9) test disks were exposed to condensing water alone, or condensing hydrogen peroxide and UV light in the test chamber. Aluminum disks painted with a two part epoxy primer and polyurethane top coat were employed. Eight of the disks were doped with PHM at approximately 10 g/m^2 (within the doped area of the disk). Six of these were further coated each with a different fumed silica powder, and one was lightly sprayed with an aqueous solution of a liquid surfactant. The ninth disk had nothing put on it, and served to test the pattern of condensation on an untreated, painted surface, and possible surface damage. A tenth disk coated with PHM only was kept outside of the test chamber in a covered container as a control.

In Table 4, all results for PHM recovered are expressed as the percentage relative to that recovered from the control disk, which had PHM applied to it, and then was kept in a covered

Table 4.

Phenyl Half-Mustard Exposed to Hydrogen Peroxide and UV Light

Experiment	G	I
Date	11-20	11-21
Phenyl Half-Mustard (g/m^2)	10	10
Liquid	H_2O	50% H_2O_2
Condensed (g/m^2)	146	146
UV Light	no	yes
Run time (min)	40	40

Results:

Disk	Surfactant	Percent PHM Recovered		I/G
1	Aerosil 200	33	10	30
2	Sipernat 22 LS	44	6	13
3	Cab-O-Sil Grade EH-5	46	6	13
4	Cab-O-Sil Grade M-5	40	15	36
5	Aerosil R974*	33	8	25
6	Cab-O-Sil TS-610*	38	6	16
7	FloMo 9N (liquid)	31	11	35
8	None	23	17	73
Control	No Surfactant	100	100	--
Reference Solution		110	109	--

*These silica powders have been treated to make them hydrophobic; the other four are hydrophyllic.

container outside of the test chamber. At the end of the run, the disks were transferred to vials that contained 15 mL of acetone, and allowed to soak briefly to dissolve residual PHM. With this protocol, 100% recovery corresponded to 67 ppm (v/v) PHM in the acetone. Preliminary tests had established that this was approximately the maximum concentration consistent with a linear response on the GC. "Reference solution" was prepared to contain 40 ppm phenyl sulfide and 67 ppm PHM. The good agreement between "Reference" and "Control" observed in all cases illustrates the basic precision of the analytical protocol, and demonstrates that PHM is recovered well from the test disks.

In Experiment I, hydrogen peroxide and UV light were used. With the three best silica powders, only 6% of the initial PHM was recovered. Part of the loss of PHM is due to evaporation. Additional agent may have been "lost" by strong adsorption on to the silica powder. The last column of Table 4 (labeled I/G) presents the percentages from Experiment I divided by the percentages from Experiment G. In effect, the effect of evaporation and possible adsorption on to the silica has been corrected for. With the three best surfactants, the amount recovered in Experiment I is only 13-16% of the amount recovered in Experiment G. Air samples taken from the test chamber during the run showed no detectable PHM nor the inferred hydrolysis product. Therefore, the part of the PHM that evaporated was destroyed in air.

Due to the incomplete evaporation of PHM using the Inconel cup, Experiment AC was done to repeat Experiment I. Experiment AC used the auxiliary heat block that was installed after experiments I and G. This allowed complete evaporation of PHM and maximum saturation of the test chamber. The results are summarized in Table 5. The auxiliary heat block makes it possible to actually see that the PHM has evaporated. In addition, while the PHM was evaporating, air samples were withdrawn from the chamber and analyzed on the GC. In Experiment AC two air samples were withdrawn from the chamber while the PHM was evaporating and before starting the peroxide and UV light.

The second air sample contained 88 mg/m^3 of PHM (total amount of PHM in the chamber air = 3.4 mg). One minute after withdrawing this sample, the hydrogen peroxide pump was started and the UV lamps turned on. A chamber air sample was taken 5 minutes later and demonstrated a PHM peak that was too small to quantitate.

Our best estimate is that it was less than 2 mg/m^3, indicating that more than 97% of the PHM present in the chamber air was destroyed within 5 minutes of starting the hydrogen peroxide and UV light.

Recovery of PHM in Experiment AC is compared with Experiment G in Table 5. The recovery of PHM in Experiment AC is slightly

Table 5.

Phenyl Half-Mustard Exposed to Hydrogen Peroxide and UV Light

Experiment	G	AC
Date	11-20	2-26
Phenyl Half-Mustard (g/m^2)	10	10
Liquid	H_2O	50% H_2O_2
Condensed (g/m^2)	146	108
UV Light	no	yes
Run time (min)	40	40

Results:

Disk	Surfactant	Percent PHM	Recovered	AC/G
1	Aerosil 200	33	9	27
2	Sipernat 22 LS	44	12	27
3	Cab-O-Sil Grade EH-5	46	8	17
4	Cab-O-Sil Grade M-5	40	12	30
5	Aerosil R974*	33	8	23
6	Cab-O-Sil TS-610*	38	14	36
7	FloMo 9N (liquid)	31	11	34
8	None	23	8	35
Control	No Surfactant	100	100	-
Reference	Solution	110	129	-

*These silica powders have been treated to make them hydrophobic; the other four are hydrophyllic.

greater than in Experiment I, because more PHM was successfully evaporated at the beginning, but with all surfactants, use of H_2O_2 and UV light greatly decreased the amount of PHM recovered.

In Experiment AC (Table 5) the effect of the fumed silica powder was uncertain; recovery of PHM from Disk 8 (no surfactant) compares favorably with the other disks. In Experiment I (Table 4) the recovery from Disk 8 was nearly three times greater than from Disks 2, 3, and 6, suggesting that the corresponding silica powders had a large beneficial effect upon the oxidation reaction.

Experiments Using Dimethoate

Dimethoate is chemically very similar to Malathion, but much more highly soluble in water. In most respects, the experiments with DMO were similar to those with Malathion and PHM. Because the vapor pressure of DMO is very low, there was no need to presaturate the chamber air with DMO, and losses by evaporation were negligible.

In Experiment L, test disks coated with DMO were exposed to condensing water vapor only with no UV light. This experiment is summarized in Table 6. The test disks were prepared and coated as in Experiments M and N described below. All results for DMO recovered are expressed as the percentage relative to that recovered from the Control disk, which had DMO applied to it, and was kept in a covered container outside of the test chamber. At the end of the run, the disks were transferred to vials that contained 10 mL of acetone with 40 ppm phenyl sulfide as an internal standard, and allowed to soak briefly to dissolve residual DMO. With this protocol, 100% recovery corresponded to 100 ppm (v/v) DMO in the acetone. Preliminary tests had established that this was within the linear response on the GC. "Reference solution" was prepared to contain 40 ppm phenyl sulfide and 100 ppm DMO. It is evident that the DMO is recovered well from the test disks, and loss by evaporation appears small. The discrepancy between "Reference" and "Control" in this experiment seems to be due to random variation in the two samples. The same ratios in the other two experiments reported here (M and N) were 1.06 and 0.95, respectively.

Experiments M and N were performed by exposing test disks coated with DMO to UV light and condensing hydrogen peroxide vapor. Aluminum disks painted with a two part epoxy primer and polyurethane top coat were employed. Five disks were doped with DMO at approximately 8 g/m^2 (within the doped area of the disk). Dimethoate was applied as a 10% solution in ethanol containing 2% glycerol. Ten microliters of this solution applied to the center of a 0.625" diameter disk typically spread to wet an area of approximately 0.50" diameter, then dried, leaving a "slick"

Table 6.

Dimethoate Exposed to Condensing Water

Experiment	L
Date	12-07
Dimethoate (g/m^2)	8
Liquid	H_2O
Condensed	146
UV Light	no
Run time (min)	40

Results:

Disk	Surfactant	%DMO Recovered (Relative to Control)
2	Sipernat 22 LS	114
3	Cab-O-Sil Grade EH-5	113
6	Cab-O-Sil TS-610*	79
8	None	116
Control	No surfactant	100
Reference Solution		123

*This silica powder is hydrophobic; the other two are hydrophyllic.

composed of DMO and glycerol which did not appear to crystallize during the duration of the experiment. Three of the disks were further coated, each disk with a different fumed silica powder. Because DMO is relatively water soluble, good mass transfer of this agent from disk to condensing hydrogen peroxide vapor should not require surfactants. Therefore, only three silica powders were tested, two hydrophilic silicas and one hydrophobic silica. Two additional disks coated with DMO only were kept outside of the test chamber in covered containers, one serving as a control and the other being lightly sprayed with deionized water to test for hydrolysis or other loss mechanism due to water alone. Experiment L, utilizing water only, demonstrated complete recovery of DMO from the test disks (Fig.2). Experiment M, utilizing 50% hydrogen peroxide and UV light, demonstrated that DMO is totally destroyed (within the limits of detection of the GC) in the test chamber (Fig.3). No detectable DMO peaks were observed after 40 minutes reaction time.

After Experiment M was completed, we devoted considerable effort to verify that the apparent destruction of DMO was not due to an analytical artifact. The solution obtained soaking the test disk in ethanol (Experiments L and M) or acetone (Experiment N) will contain some residual hydrogen peroxide as well; might not the hydrogen peroxide continue to react with the DMO after the experiment proper has been completed? In ancillary experiments designed to test this hypothesis, we added realistic amounts of hydrogen peroxide to known concentrations of DMO in ethanol or acetone (one drop of 50% H_2O_2 added to 10 mL of solvent in the vial corresponds to the amount of H_2O_2 remaining on the disk at the end of the experiment). A loss of 25% was observed with a reference solution containing 100 ppm DMO, and the loss was 80-100% for a reference solution containing 10 ppm DMO. In other words, under the conditions of Experiment M, the lower detection limit for residual DMO was effectively 10% of the amount initially applied.

The percentage of DMO recovered did not increase with time after adding the hydrogen peroxide; apparently, the DMO was lost by reaction with hydrogen peroxide in the injector of the GC. Part of the problem was traced to an improperly packed GC column. After the column was repaired, the loss was smaller but still significant.

It was reasoned that adding a proper anti-oxidant to act as a competing substrate for reaction with hydrogen peroxide should diminish the loss of DMO. It was quickly established that adding 100 ppm alpha-monothioglycerol to the solvent used to extract the disks enabled good recovery of DMO at the 10 ppm level, although at the cost of a "dirty" baseline, and some new peaks related to the anti-oxidant. Subsequently, we used acetone containing 40ppm

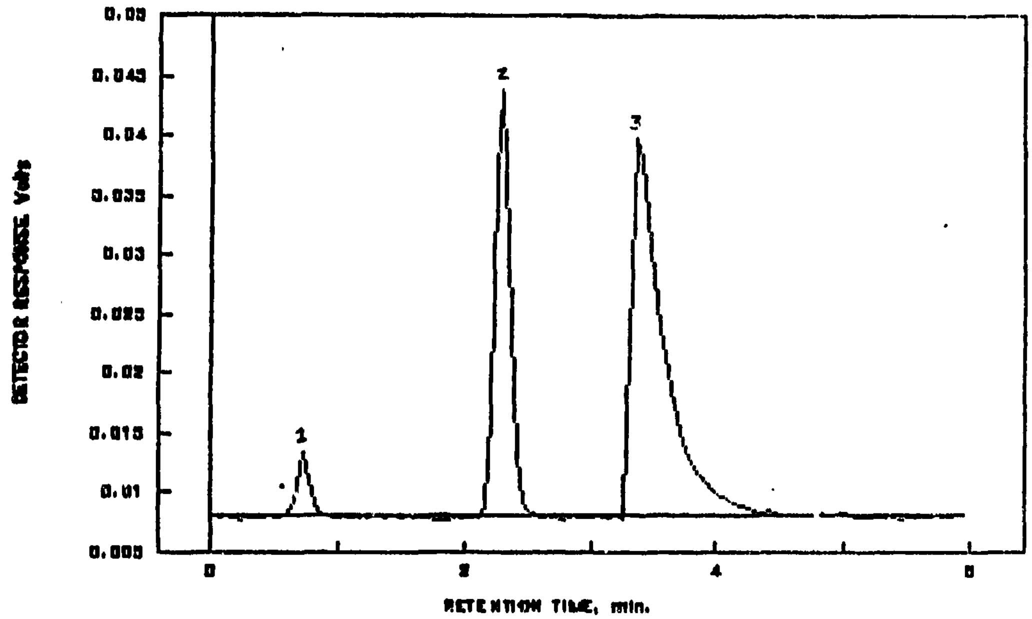


Fig.2. Experiment L, Water Only, No UV. Peak 1 = Acetone; Peak 2 = Phenyl Sulfide; Peak 3 = Dimethoate.

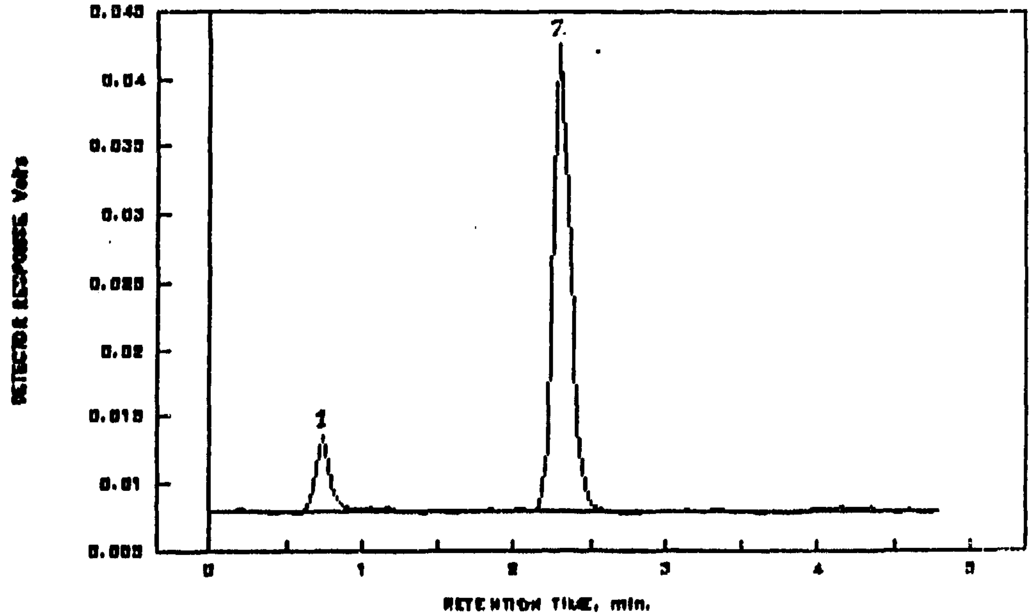


Fig.3. Experiment M, 50% Hydrogen Peroxide and UV. Peak 1 = Acetone; Peak 2 = Phenyl Sulfide; Dimethoate destroyed.

phenyl sulfide (internal standard) plus 100 ppm alpha-monothioglycerol as the solvent for extracting the test disks. It is necessary to add the monothioglycerol to the solvent immediately before use, because once in solution, the monothioglycerol slowly oxidizes (probably dimerizing), to produce a peak at about 5.2 minutes on the GC.

Additional experiments established that hydrogen peroxide does not interfere with recovery of either Malathion or PHM; therefore, this problem did not place the results for those agents in doubt.

Experiment N was done as a repeat of Experiment M to verify the observed results. Experiment N differed from Experiment M only in the analytical procedure used: acetone was used, and 100 ppm monothioglycerol was added to it. Figure 4 is a chromatogram of a sample disk from inside the chamber after 40 minutes of exposure to condensing hydrogen peroxide vapor and UV light. The baseline is somewhat dirty, but there is no peak in the position of DMO. Gas chromatograms obtained from all disks that had been exposed inside the chamber looked like this, with no DMO peak. Recovery of DMO from samples spiked with DMO and hydrogen peroxide was good; therefore, the DMO really was destroyed to below the limit of detection. A large new peak appeared at about 5.2 minutes. This peak was completely absent from the samples exposed in Experiment M; for that reason, it is unlikely to represent a product of the oxidation of DMO. A peak in exactly the same position, albeit smaller, *is* present in a sample where solvent containing phenyl sulfide and monothioglycerol was spiked with a drop of hydrogen peroxide (Fig. 5); most likely, the new peak represents a product of oxidation of monothioglycerol, probably the oxidative dimer.

Experiments Using DIMP

Diisopropyl methylphosphonate is quite volatile, and is a simulant for GB. Using DIMP as the agent simulant we attempted to estimate the rate of destruction of GB in air when exposed to hydrogen peroxide vapor and UV light.

It was calculated that 60 mg of DIMP evaporated on the chamber's auxiliary heat block would produce a concentration in the chamber air of 0.15 μg per 100 μL assuming complete volatilization. This would be equivalent to a 1 μL liquid GC injection of a 150 ppm sample. For our GC conditions, 150 ppm is at the upper limit of linearity. The heat block was turned on and the DIMP added. The chamber door was closed and taped shut to minimize air leakage and the pump started using either deionized water without UV light or 50% hydrogen peroxide with UV light. Sampling started immediately and continued periodically for the duration of the experiment. 100 μL gas samples were withdrawn from the chamber

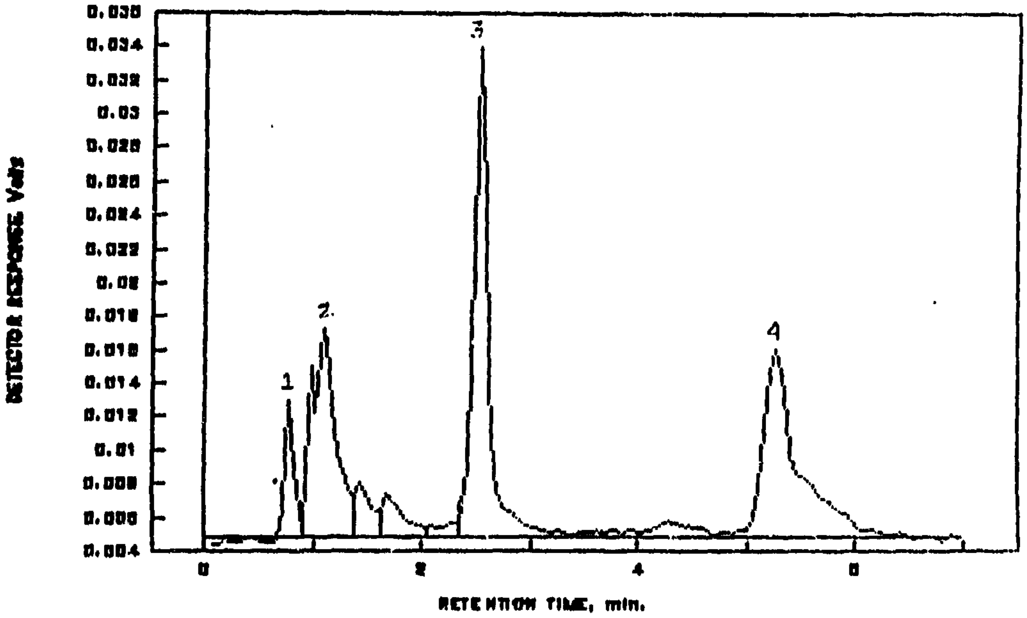


Fig.4. Experiment N, 50% Hydrogen Peroxide and UV. α-Monothioglycerol Added to Samples Immediately Prior to GC Injection. Peak 1 = Acetone; Peak 2 = α-monothioglycerol; Peak 3 = Phenyl Sulfide; Peak 4 = α-monothioglycerol decomposition product.

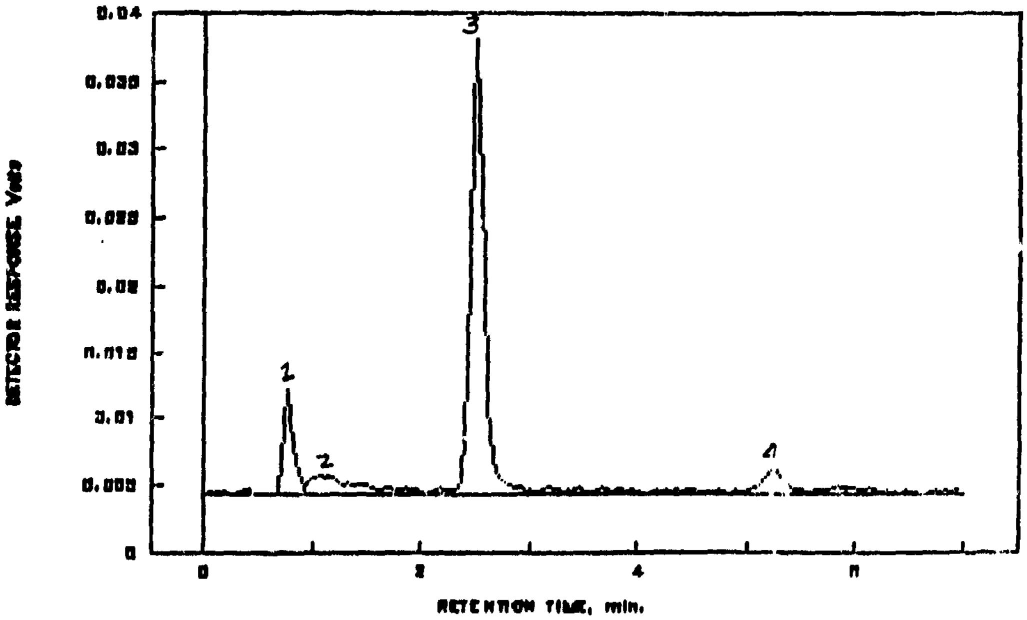


Fig.5. Sample of 40 ppm Phenyl Sulfide and 100 ppm α-Monothioglycerol in Acetone Spiked with One Drop of 50% Hydrogen Peroxid3. Peak 1 = Acetone; Peak 2 = α-monothioglycerol; Peak 3 = Phenyl Sulfide; Peak 4 = α-mono-thioglycerol decomposition product.

using a 1.0 mL Hamilton Gas-tight syringe. The samples were immediately analysed by GC using the FPD with the phosphorus filter installed.

The first two experiments using DIMP were Experiment W which used deionized water without UV light and Experiment X which used 50% hydrogen peroxide with UV light. The results are summarized in Table 7. The data demonstrate a significant loss of DIMP in both experiments. This was originally attributed to either the loss of DIMP through leakage from the chamber or reaction with water alone. The UV light and hydrogen peroxide was more effective than water at removing DIMP as the concentration of DIMP in the reaction chamber decreased.

Experiment AA was set up to address the problem regarding the loss of DIMP in both experiments and the results are shown in Table 8a. In Experiment AA 60 mg of DIMP was evaporated in the chamber, but neither water, peroxide nor UV light was utilized for the first 40 minutes. Air samples were regularly drawn for analysis. The results demonstrated that leakage from the chamber did gradually decrease the concentration of DIMP in the chamber, but the decrease was quite slow, much less than had been observed in Experiment W. Condensation of DIMP on the internal surfaces of the test chamber may also have contributed to this decrease. After 40 minutes the pump was started with water and the DIMP concentration quickly dropped. The pump was stopped after 30 minutes, the chamber opened, and some of the condensate on the floor of the chamber was drawn up, diluted 1:100 in acetone and 1 µL analysed on the GC. This resulted in a dilution corrected value of 1810 ppm DIMP which demonstrated that the DIMP vapor was dissolving in the water condensate. Based on the amount of water pumped during the experiment this would represent approximately 44 mg, or almost 75% of the DIMP originally evaporated. It is clear that most of the decrease in DIMP concentration in air with condensing water was due to dissolution of DIMP in the water condensate that formed.

Experiment AG was set up similar to Experiment AA, but using 50% H_2O_2 instead of H_2O. Three blank test disks were placed in the test chamber. The experiment was started with the hydrogen peroxide feed pump off, and the UV lamps off. DIMP (60 mg) was evaporated on the auxilliary heat block over a period of 19 minutes, at which time the concentration of DIMP in the chamber air was constant. At time = 19 minutes, the 50% H_2O_2 pump was started, and the UV lamps were turned on. The experiment was terminated at t = 52 minutes. At the end of the experiment the disks were placed in acetone to recover DIMP that had condensed upon them (with water and H_2O_2), and the extracts were assayed on the GC. The total amount of DIMP that condensed within the

Table 7.

Sample Data from DIMP Experiments W and X

Experiment W (with H_2O)		Experiment X (with H_2O_2)	
Time sample taken after start of Expt. (mins)	DIMP (ppm)	Time sample taken after start of Expt. (mins)	DIMP (ppm)
2	1.28	1	1.67
7	3.27	5	4.85
10	4.59	8	4.74
15	3.23	11	4.27
20	2.37	15	2.24
25	1.52	20	1.33
30	1.32	25	1.01
35	1.41	30	1.07
40	1.26	35	0.75
		40	0.79

Table 8a.

Sample Data from DIMP Experiment AA.
(First 40 minutes uses no condensing
Vapor. At T = 40 mins H_2O is started.)

Time sample taken after start of Exp. AA (mins)	DIMP (ppm)	% Change
1	0.91	--
6	42.23	+4541
10	96.20	+ 128
15	67.71	- 30
20	61.07	- 10
30	53.70	- 12
40	33.42	- 38
40	Start pumping H_2O	
45	8.16	- 76
60	4.72	- 42
70	2.52	- 47

Total run time = 70 minutes.

Data from GC analysis of condensate from chamber floor.
Total H_2O_2 pumped during experiment = 24.3 mL.

Assayed Conc.of DIMP (ppm)	Dilution Factor	Dilution Corr. Conc. of DIMP (ppm)	Total DIMP in Condensate	Percent of Total DIMP
18.1	100	1810	44.0 mg	73.3%

Table 8b.

Sample data from DIMP Experiment AG.
(First 19 minutes uses no condensing vapor.
At T = 19 mins. H_2O_2 and UV are started)

Time sample taken after start of Exp.AG (mins.)	DIMP (ppm)	% Change
0	UV off, pump off.	
7	41.8	
12	43.8	+ 5
18	48.6	+ 11
19	UV on, start pumping H_2O_2.	
24	6.3	- 87
30	4.2	- 33
37	1.7	- 60
52	1.1	- 35

Total run time = 52 minutes.

Data from GC analysis of condensate on blank disks.
Volume of condensate on each disk = 0.0287 mL.
Total H_2O_2 pumped during experiment = 32.4 mL.

Disk#	Assayed Conc.of DIMP (ppm)	Dilution Factor	Dilution Corrected Conc. of DIMP (ppm)	Total DIMP in Condensate	Percent of Total DIMP
1	3.04	174	529	17.1 mg	28.5%
2	3.56	174	619	20.1 mg	33.5%
3	4.58	100	458	14.8 mg	24.7%
Mean			535	17.3 mg	28.8%

chamber and remained at the end of the experiment was then calculated using the result of the assay, the area of the disks ($0.31\ in^2$), the area of the floor of the chamber ($192.5\ in^2$), the volume of hydrogen peroxide pumped (32.4 mL), and the previously determined fact that approximately 55% of the condensate forms on the floor of the chamber. The results are shown in Table 8b. The concentration of DIMP in the chamber air drops more rapidly when using H_2O_2 and UV light than with H_2O, and the amount of DIMP in the condensate with hydrogen peroxide (expressed as the percentage of the initial 60 mg of DIMP evaporated) is considerably less than in the condensed water, 29% vs. 74%. This indicates that the combination of hydrogen peroxide and UV light is effectively destroying the DIMP and that a longer reaction time should result in complete destruction. Total time available for the reaction in this experiment was only 33 minutes.

Experiments Using Catalytic Surfaces

Thirteen metal oxides and two metal sulfides were tested for their ability to catalyze the reaction of agent simulants with H_2O_2. The sulfides were also tested in combination with calcium carbonate. To apply these compounds to the test disks the disks were first painted with a two-part epoxy primer (MIL-P-233377E) and allowed to dry. Then they were sprayed with the polyurethane top coat (MIL-C-53039). When the sheen of the top coat disappeared, which takes about 10 minutes, the disk was dropped, top-side down, into a large-mouth vial containing one of the oxides or sulfides of interest in powdered form. The vial was gently swirled and shaken to allow the powder to adhere to the tacky top coat. The disk was removed and set aside to completely dry. The following day the disks were brushed to remove loose powder and the edges sanded so that only the top surface of each disk is coated.

The first set of experiments reported here used the insecticide DMO as agent simulant. The DMO has a water solubility of 2.5% at room temperature that makes it a good match for VX and GD and its low volatility (10^{-8} bar at 20°C) means that there is practically no loss due to evaporation during the experiments. Disks were doped with 10 uL of a 10% solution of DMO in ethanol + 2% glycerol. When the DMO is applied it typically spreads rapidly over the entire surface of the oxide or sulfide coated disks resulting in approximately 8 g/m^2 DMO (within the doped area of the disk). The DMO does not spread out unaided over the surface of those disks not coated with one of the powders, but must be manually spread. Each experiment examined two of the potential catalysts and included uncoated control disks used to determine what effect H_2O_2 alone had on the agent simulant. Duplicate

disks of each type were exposed to 50% hydrogen peroxide condensing vapor within the reaction chamber. Single disks of each catalyst being tested and an uncoated disk were kept in a covered petri dish outside of the chamber during the course of the experiment. The uncoated disk served as the assay control, whereas the coated disks served as standards of comparison for those disks that were coated with the same surface catalyst and exposed to H_2O_2 vapor. Additionally, any reaction occurring between the agent simulant and the coated material in the absence of UV light is evidenced by comparing the coated disks that were outside the chamber with the uncoated assay control disk.

Disks were exposed in the chamber for 40 minutes. At the conclusion of each experiment the disks were transferred to vials that contained 10 mL of acetone with 40 ppm of phenyl sulfide as an internal standard for GC analysis. The disks were soaked for 15-20 minutes to dissolve residual DMO. 100% recovery corresponded to 100 ppm (v/v) DMO in the acetone. Reference solution was prepared to contain 40 ppm phenyl sulfide and 100 ppm DMO. All samples that were exposed to H_2O_2 condensing vapor had alpha-monothioglycerol added as an anti-oxidant immediately prior to GC analysis. Results are expressed as %DMO recovered relative to the uncoated control disk that had DMO applied to it, and was kept in a covered container outside of the chamber.

Ten experiments (Tables 9a-j) were performed to test the various compounds. These ten experiments are summarized in Table 10. The %DMO recovered ranged from 3.7 to 105%. Eighteen uncoated disks that were run during these experiments demonstrated a mean recovery of 57%, with a range of 39 to 82%, suggesting that an average of 43% of the DMO is destroyed by exposure to 50% hydrogen peroxide vapor alone. Recoveries of greater than 57% were observed for six of the tested materials meaning these materials, in effect, were protecting the agent simulant. The highest observed recoveries of 103 and 91% were attained with manganese (IV) dioxide and lead (II,III) oxide (Pb_3O_4), respectively. During the course of their exposure to hydrogen peroxide condensing vapor, no condensation formed on their surfaces. Apparently, they are such strong catalysts for decomposition of H_2O_2 that the hydrogen peroxide is completely and immediately destroyed on contact with the disk surface leaving these disks totally dry and thereby preventing reaction. Other unsuccessful catalysts were lead titanate ($PbTiO_3$), 71% recovery, nickel (II) oxide (NiO), 67%, manganese (II,III) oxide (Mn_3O_4), 62%, and manganese (II) oxide (MnO), 59%.

The ability of five of the tested compounds to enhance the destruction of DMO was judged possibly effective. The percent

Table 9a.

Experiment O, 12-28-90,
50% H_2O_2, No UV Light, Run Time = 40 Min

Disk#	Catalyst	% DMO Recovered (relative to control)
1	Fe_2O_3	52
2	Fe_2O_3	47
4	MnO_2	101
5	MnO_2	105
7	None	82
8	None	57
Control	None	100
Fe_2O_3 Std.	Fe_2O_3	100
MnO_2 Std.	MnO_2	117
Reference		140

Table 9b.

Experiment P, 1-07-91,
50% H_2O_2, No UV Light, Run Time = 40 Min

Disk#	Catalyst	%DMO Recovered (relative to control)
1	Cr_2O_3	46
2	Cr_2O_3	42
4	CuO	30
5	CuO	32
7	None	46
8	None	48
Control	None	100
Cr_2O_3 Std.	Cr_2O_3	80
CuO Std.	CuO	82
Reference		86

Table 9c.

Experiment Q, 1-07-91,
50% H_2O_2, No UV Light, Run Time = 40 Min

Disk#	Catalyst	% DMO Recovered (relative to control)
1	NiO	67
2	NiO	66
4	Co_3O_4	56
5	Co_3O_4	58
7	None	59
8	None	67
Control	None	100
NiO Std.	NiO	102
Co_3O_4 Std.	Co_3O_4	106
Reference		105

Table 9d.

Experiment R, 1-08-91,
50% H_2O_2, No UV Light, Run Time = 40 Min

Disk#	Catalyst	%DMO Recovered (relative to control)
1	Pb_3O_4	92
2	Pb_3O_4	89
4	$PbTiO_3$	71
5	$PbTiO_3$	71
7	None	60
8	None	--
Control	None	100
Pb_3O_4 Std.	Pb_3O_4	80
$PbTiO_3$ Std.	$PbTiO_3$	96
Reference		78

Table 9e.

Experiment S, 1-08-91,
50% H_2O_2, No UV Light, Run Time = 40 Min

Disk#	Catalyst	% DMO Recovered (relative to control)
1	Fe_2O_3	46
2	Fe_2O_3	50
4	Fe_3O_4	47
5	Fe_3O_4	57
7	None	62
8	None	--
Control	None	100
Fe_2O_3 Std.	Fe_2O_3	97
Fe_3O_4 Std.	Fe_3O_4	101
Reference		92

Table 9f.

Experiment T, 1-09-91,
50% H_2O_2, No UV Light, Run Time = 40 Min

Disk#	Catalyst	%DMO Recovered (relative to control)
1	Ag_2O	5.4
2	Ag_2O	10.1
4	$FeTiO_3$	56
5	$FeTiO_3$	48
7	None	55
8	None	56
Control	None	100
Ag_2O Std.	Ag_2O	44
$FeTiO_3$ Std.	$FeTiO_3$	100
Reference		87

Table 9g.

Experiment U, 1-09-91,
50% H_2O_2, No UV Light, Run Time = 40 Min

Disk#	Catalyst	% DMO Recovered (relative to control)
1	MnO	53
2	MnO	65
4	Mn_3O_4	63
5	Mn_3O_4	60
7	None	57
8	None	60
Control	None	100
MnO Std.	MnO	92
Mn_3O_4 Std.	Mn_3O_4	89
Reference		88

Table 9h.

Experiment Y, 1-21-91,
50% H_2O_2, No UV Light, Run Time = 40 Min

Disk#	Catalyst	%DMO Recovered (relative to control)
1	$Ag_2S/CaCO_3$	37
2	$Ag_2S/CaCO_3$	34
4	Ag_2S	38
5	Ag_2S	40
7	None	48
8	None	39
Control	None	100
$Ag_2S/CaCO_3$ Std.	$Ag_2S/CaCO_3$	103
Ag_2S Std.	Ag_2S	100
Reference		96

Table 9i.

Experiment Z, 1-21-91,
50% H_2O_2, No UV Light, Run Time = 40 Min

Disk#	Catalyst	% DMO Recovered (relative to control)
1	FeS_2	3.7
2	FeS_2	8.3
4	$FeS_2/CaCO_3$	35
5	$FeS_2/CaCO_3$	31
7	None	58
8	None	59
Control	None	100
FeS_2 Std.	FeS_2	95
$FeS_2/CaCO_3$ Std.	$FeS_2/CaCO_3$	103
Reference		113

Table 9j.

Experiment AB, 2-25-91,
50% H_2O_2, No UV Light, Run Time = 40 Min

Disk#	Catalyst	% DMO Recovered (relative to control)
1	$Fe(OH)_3$	31
2	$Fe(OH)_3$	33
4	$FeCO_3$	33
5	$FeCO_3$	44
7	None	50
8	None	60
Control	None	100
$Fe(OH)_3$ Std.	$Fe(OH)_3$	88
$FeCO_3$ Std.	$FeCO_3$	93
Reference		99

Table 10.

Summary of Experiments Utilizing Metal Oxides/Sulfides

Date	Exp.	Catalyst	No.of uncoated Disks	With H_2O_2 Mean % DMO Recovered (relative to uncoated control)	No H_2O_2 % DMO Recovered (relative to control)*
12-28	O	Fe_2O_3	2	49	99
1-08	S	Fe_2O_3	2	48	97
12-28	O	MnO_2	2	103	117
1-07	P	Cr_2O_3	2	44	80
1-07	P	CuO	2	31	82
1-07	Q	NiO	2	67	102
1-07	Q	Co_3O_4	2	57	106
1-08	R	Pb_3O_4	2	91	80
1-08	R	$PbTiO_3$	2	71	96
1-08	S	Fe_3O_4	2	52	101
1-09	T	Ag_2O	2	7.8	44
1-09	T	$FeTiO_3$	2	52	100
1-09	U	MnO	2	59	92
1-09	U	Mn_3O_4	2	62	89
1-21	Y	$Ag_2S/CaCO_3$	2	36	103
1-21	Y	Ag_2S	2	39	100
1-21	Z	FeS_2	2	6.0	95
1-21	Z	$FeS_2/CaCO_3$	2	33	103
2-25	AB	$Fe(OH)_3$	2	32	88
2-25	AB	$FeCO_3$	2	39	93
Uncoated Disks			18	57	

*All values in this column have N=1.

recovery of DMO in each case was in the bottom of the control range and less than the individual control recovery for each experiment. These included cobalt (II,III) oxide (Co_3O_4), 57% recovery, iron titanate ($FeTiO_3$), 52%, iron (II,III) oxide (Fe_3O_4), 52%, iron (III) oxide (Fe_2O_3), 49%, and chromium (III) oxide (Cr_2O_3), 44%.

The remaining compounds and their percent recoveries of DMO were silver sulfide (Ag_2S), 39%, siderite ($FeCO_3$), 39%, silver sulfide/calcium carbonate, 36%, pyrite (FeS_2)/Calcium carbonate (33%), ferric hydroxide ($Fe(OH)_3$), 32%, copper (II) oxide (CuO), 31%, silver (I) oxide (Ag_2O), 7.8%, and pyrite (FeS_2), 6.0%. The significant reduction in recovery for Ag_2O and FeS_2 must be considered with caution. In both Experiment T (Ag_2O) and Experiment Z (FeS_2) the coating on the disks had left a residue on the floor of the reaction chamber at the completion of each experiment. Obviously, some DMO was lost in this manner. Though some loss with these particulates is likely, we doubt that this was the major loss mechanism. The effect of Ag_2O on the agent simulant is of interest. In Experiment T, the Ag_2O control disk that was outside of the reaction chamber demonstrated a 44% recovery of DMO. That Ag_2O had catalyzed the decomposition of DMO without exposure to hydrogen peroxide provided credibility to the 7.8% recovery observed on the Ag_2O coated disks that were exposed to peroxide. This was expected since silver is strongly reactive with sulfur compounds, such as DMO.

The second set of experiments reported here used PHM as the agent simulant. Some loss of PHM due to evaporation from the disks is expected, but can be accounted for. As in previously described experiments employing PHM, 0.06 mL of PHM was evaporated on the auxiliary heat block prior to starting the 50% H_2O_2. The concentration of PHM in the chamber air was monitored in each experiment and the experiment was begun when the concentration in the air began to decline, due to air leakage from the chamber and condensation upon the walls. The concentration of PHM in the chamber air dropped rapidly once the hydrogen peroxide was started, but not as quickly as it did when both hydrogen peroxide and UV light were used. In the first five minutes approximately 75% of the PHM was destroyed by hydrogen peroxide alone compared to more than 95% when hydrogen peroxide and UV were employed. The experiments using catalytic surfaces and PHM were set up identically to those which used DMO. Disks were doped with 1 µL

of PHM which resulted in 10 g/m^2 PHM (within the doped area of the disk). On completion of each experiment the disks were soaked for 15-20 minutes in 15 mL acetone that contained 40 ppm phenyl sulfide (PS) as internal standard. A recovery of 100% corresponds to 67 ppm PHM. The reference solution was prepared that contained 67 ppm PHM + 40 ppm PS. Results are expressed as %PHM recovered relative to the uncoated control disk that had PHM applied to it and was kept in a covered container outside of the reaction chamber.

Three experiments were done (Tables 11a-c.) to test six of the compounds that were effective at destroying DMO to determine if they were also effective at destroying PHM. The six catalytic surfaces tested and the %PHM recovered were copper oxide, 32%, ferric hydroxide, 34%, pyrite/calcium carbonate, 23%, pyrite, 30%, silver oxide, 55%, and silver sulfide/calcium carbonate, 35%. These results are summarized in Table 12.

Six uncoated disks that were run during the course of these experiments demonstrated a mean recovery of 32% with a range of 29 to 36%. This compares to a mean recovery of 57% using DMO. The difference can be attributed to either evaporation or the uncatalyzed destruction of PHM by hydrogen peroxide. Of the six catalytic surfaces tested only the pyrite and pyrite/calcium carbonate treated disks demonstrated an enhanced ability to destroy PHM. Silver sulfide, copper oxide and ferric hydroxide were all comparable to the uncoated disks. The effect of the silver oxide on the PHM was directly opposite to its effect on DMO. Whereas silver oxide was highly effective in destroying DMO both with and without hydrogen peroxide, it actually protected the PHM. The lower water solubility of PHM limits the rate of mass transfer of PHM into the condensing hydrogen peroxide which explains the greater effectiveness of some of these compounds on DMO. However, the silver oxide effect indicates another process is going on to somehow protect the agent simulant, otherwise, the percent recovery should be no higher than the uncoated disk.

<u>Experiments on Survivability of Some Conformal Coatings</u>

A decontamination process must not damage electronic equipment. The critical component that must not be damaged is the conformal coating that protects the circuit boards. Several small test boards constructed to military specifications, and coated with a variety of Mil-Spec, UV-cured conformal coatings (Table 13) were obtained form Dr. Olexander Hnojewyj of Litton Applied Technologies and evaluated for their ability to withstand exposure to 50% hydrogen peroxide condensing vapor. These coatings were not exposed to UV light because, in the field, the UV light used in the decontamination system would not reach the coated electronic components.

Table 11a.

Experiment AD, 3-01-91,
50% H_2O_2, No UV Light, Run Time = 40 Min

Disk#	Catalyst	% DMO Recovered (relative to control)
1	Ag_2O	56
2	Ag_2O	54
4	$Ag_2S/CaCO_3$	38
5	$Ag_2S/CaCO_3$	32
7	None	29
8	None	29
Control	None	100
Ag_2O Std.	Ag_3O	104
$Ag_2O/CaCO_3$ Std.	$Ag_2S/CaCO_3$	125
Reference		101

Table 11b.

Experiment AE, 3-04-91,
50% H_2O_2, No UV Light, Run Time = 40 min

Disk#	Catalyst	% DMO Recovered (relative to control)
1	CuO	29
2	CuO	35
4	$Fe(OH)_3$	33
5	$Fe(OH)_3$	34
7	None	32
8	None	33
Control	None	100
CuO Std.	CuO	102
$Fe(OH)_3$ Std.	$Fe(OH)_3$	108
Reference		107

Table 11c.

Experiment AF, 3-04-91,
50% H_2O_2, No UV Light, Run Time = 40 Min

Disk#	Catalyst	% DMO Recovered (relative to control)
1	$FeS_2/CaCO_3$	20
2	$FeS_2/CaCO_3$	26
4	FeS_2	30
5	FeS_2	29
7	None	32
8	None	36
Control	None	100
$FeS_2/CaCO_3$ Std.	$FeS_2/CaCO_3$	103
FeS_2 Stds	FeS_2	106
Reference		107

Table 12.

Summary of Experiments Evaluating Catalytic Oxides/Sulfides

				With H_2O_2	No H_2O_2
Date	Exp.	Catalyst	No.of uncoated Disks	Mean % PHM Recovered (relative to uncoated control)	% PHM Recovered (relative to control)*
3-01	AD	Ag_2O	2	55	104
3-01	AD	$Ag_2S/CaCO_3$	2	35	125
3-04	AE	CuO	2	32	102
3-04	AE	$Fe(OH)_3$	2	34	108
3-04	AF	$FeS_2/CaCO_3$	2	23	103
3-04	AF	FeS_2	2	30	106
Uncoated Disks			6	32	

*All values in this column have N=1.

Table 13.

Conformal Coatings Tested for Resistance to Hydrogen Peroxide

Conformal Coating*	Type	Total Exposure (min)	Total Relative Damage**
Dymax Multi-Cure 984	UR	40	++
Dymax Multi-Cure 984?	UR	40	+++
Dymax Multi-Cure 984F	UR	120	++++
Union Carbide Envibar	ER	40	++++
Union Carbide Envibar	ER	40	++++++
Loctite Shadow Cure 361	UR	40	++
W.R.Grace UV-920	AR	160	+
Westinghouse B-566	AR,ER,UR	80	++
Dow X3-6765	SR	200	-
Dow X3-6765	SR	40	++++

ER = Epoxy; AR = Acrylic; UR = Polyurethan; SR = Silicone.

*Differences between circuit boards with the same conformal coating material are due to differences in the application procedure.

**(-) indicates no damage observed. (+) signs indicate damage. The more (+) signs the greater the degree of damage to the coating.

Six conformal coatings on ten circuit boards have been tested in our reaction chamber. The board or boards are stood upright against the rear wall of the chamber for the duration of an experiment (40 minutes). At the conclusion of each experiment the board is removed, rinsed in tap water, dried and visually examined for evidence of damage. Of the six coatings tested significant damage was noted after one 40 minute exposure in the 'Envibar', 'Multi-Cure 984F', and 'Shadow Cure 361' conformal coatings, produced by Union Carbide, Dymax, and Loctite, respectively. The coating was blistered, with the blisters concentrated along solder traces and on the surfaces of coated ceramic IC's. Apparently, the hydrogen peroxide diffused through the coating and decomposed to form oxygen bubbles upon contact with solder or other materials that catalyze the decomposition of H_2O_2.

Two of the coatings tested, 'UV-920' from W.R. Grace and 'B-566' from Westinghouse, displayed minimal damage. The 'UV-920' underwent four 40 minute exposures and the 'B-566' underwent two 40 minute exposures. The same type of blistering that was observed on the coatings discussed above was present, but to a much lesser degree.

The sixth coating evaluated was 'X3-6765' from DOW. After five 40 minute exposures no damage was observed. At the conclusion of each 40 minute exposure this particular circuit board was virtually dry. It appears that something in or on the coating catalyzes the total decomposition of the peroxide and it can not then diffuse into the coating. This is an effect similar to that observed with manganese dioxide and lead oxide coated disks. The 'UV-920' coating exhibits this behaviour to a lesser degree. A second circuit board coated with 'X3-6765' conformal coating was tested and showed significant damage after one 40 minute exposure. The coatings were applied by slightly different application methods. The coating that was damaged by exposure to H_2O_2 had been applied without heating the liquid to decrease its viscosity, and with a slower belt speed in the coating apparatus.

SUMMARY

The combination of UV light and condensing hydrogen peroxide is able to destroy a large fraction of Malathion and PHM spread on a painted metal surface at about 10 g/m^2. Dusting the surface with fumed silica powders enhances the rate of reaction. This effect is pronounced, especially considering that the amount of silica powder actually adhering to the disks probably amounts to only 10-20% of the weight of the agent simulant present. In some cases, the fraction of agent simulant recovered at the end of the

experiment was as low as 6% of the amount initially applied to the test disk, but in no case was Malathion or PHM completely destroyed.

Malathion and PHM both have low solubility in water, and probably low solubility in 50% H_2O_2 as well. The rate of reaction probably is limited by the rate of mass transfer of the agent simulant into the water-like hydrogen peroxide condensate. The effect of the silica powders is consistent with this explanation. That PHM is destroyed more rapidly than Malathion is consistent with the smaller molecular weight of PHM (172.7 vs. 330) and probably faster mass transfer kinetics. Also, PHM is much more volatile than Malathion, and the PHM that evaporates is destroyed in the vapor phase.

To within our analytical limit of detection, Dimethoate at 8 g/m^2 is completely destroyed by the combination of UV light and condensing hydrogen peroxide. Forty minutes of reaction is sufficient and shorter times may be adequate. Silica powder is not needed to enhance mass transfer with DMO, and had no noticeable effect upon the results obtained.

In its chemical structure, DMO closely resembles Malathion, but DMO is much more soluble in water. Because of its greater solubility, mass transfer does not limit the rate of reaction of DMO, and apparently complete decontamination is achieved.

Among the metal oxides and sulfides tested for their ability to catalyze the reaction of DMO with hydrogen peroxide, silver (I) oxide and FeS_2 had the most effect, with 92 and 94% of the DMO gone. Silver oxide is the most soluble of the oxides tested. FeS_2 is oxidized by hydrogen peroxide, releasing soluble iron sulfate to solution in the condensate. In both cases, it is likely that the corresponding metal ion catalyzed a reaction between H_2O_2 and agent simulant dissolved in the condensate. Silver and iron are effective redox catalysts in aqueous solution, because they cycle between oxidation states. In weakly acid solution iron catalyzes the decomposition of H_2O_2 with (partial) formation of hydroxyl radical, so-called *Fenton's Reaction*. Adding calcium carbonate to the iron sulfide blocks the catalytic effect of iron. Calcium carbonate neutralizes the sulfuric acid produced by oxidation of the sulfide, and maintains a weakly basic pH in the condensate, which is unfavorable to Fenton's Reaction. Neither silver oxide nor iron sulfide had a significant effect upon the oxidation of PHM, probably because the aqueous solubility of PHM is too low. Several compounds (CuO, $FeCO_3$, Ag_2S, $Fe(OH)_3$, $Ag_2S/CaCO_3$, and $FeS_2/CaCO_3$) all

produced marginal decreases in DMO recovery and no decreases in PHM recovery. None of the other oxides tested had a significant effect upon the rate of oxidation of either agent simulant.

Five conformal coatings were tested for their resistance to damage by condensing 50% hydrogen peroxide. One coating (Dow X3-6765) suffered no visible damage after 200 minutes of exposure, if applied in a particular manner. The same coating applied in a slightly different manner was damaged. Two other coatings suffered minor damage after 160 minutes of exposure. The remaining two coatings suffered extensive damage after relatively brief exposure. In most cases, the damage was associated with formation of gas bubbles underneath the coating. Most extensive blistering occurred at the solder traces on the boards. Very likely, the lead in the solder catalyzed decomposition of hydrogen peroxide that diffused through the coating, producing oxygen bubbles.

The resistance of Mil-Spec paints to the process conditions was similarly variable. The aluminum coating system showed good resistance, while the steel coating system was severely damaged. The damage in the latter case was to the primer, which was pigmented with iron oxide.

CONCLUSIONS

The combination of condensing 50% hydrogen peroxide vapor and 254 nm UV light is able to destroy all of the agent simulants tested. The destruction of DMO is complete, due to its relatively high solubility in water. The same would probably be true of agent VX, which is also a sulfur compound with comparable water solubility. The destruction of Malathion and phenyl half-mustard is incomplete, because they are much less soluble in the condensate. The same would probably be true of sulfur mustard.

It must be noted that the 10 g/m^2 simulant loading used in our experiments is quite high; at a lower threat level, or allowing longer reaction time, complete decontamination is to be expected.

Diisopropylmethylphosphonate, a simulant for agents GB and GD, is destroyed both in the vapor phase and after it condenses and dissolves in the hydrogen peroxide condensate. The rate of reaction is slower than with Dimethoate (in the condensate) and slower than with PHM (in the gas phase), probably because DIMP is neither a sulfur compound nor an aromatic, and therefore is a less reactive substrate for hydroxyl radical.

No true solid catalyst for the reaction was identified. Silver(I) oxide and FeS_2 seem to catalyze the destruction of

Dimethoate, but the reaction probably involves the corresponding metal ions dissolved in the condensate.

The results in regard to material damage are similarly spotty. Some paints and conformal coatings have good resistance to the process conditions, while others are quickly and severely damaged.

The dithiophosphate insecticide Dimethoate has been used as a simulant for Agent VX. Dimethoate is closely related to Malathion in its chemical structure, but has a water solubility of about 2.5%, similar to VX. For this reason, we believe that Dimethoate is a superior simulant for Agent VX. Also, Dimethoate is no harder to analyze than Malathion. We recommend its further evaluation and use as a simulant for VX.

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